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(54) Title: TRANSITION METAL OLEFIN POLYMERIZATION CATALYSTS (57) Abstract This invention relates to non-Group 4 transition metal compositions useful as olefin polymerization catalysts, wherein the transition metal is in a high oxidation state. The invention further relates to design of new ligand systems and methods of preparing and using the same. Compositions useful as catalyst precursors are neutral transition metal complexes comprising the unique ligand systems of the invention. The inventive compositions may be activated to a catalytic state by ion-exchange reagents or by Lewis acids.		

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5 TITLE: Transition Metal Olefin Polymerization Catalysts

Cross Reference to Related Applications

10 This application is a Continuation-In-Part to United States Serial
Number 907,098, filed on July 1, 1992.

Field of the Invention

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 This invention relates to transition metal polymerization catalyst
systems from Groups 5-10, wherein the active transition metal center is in a
high oxidation state and stabilized by low coordination number polyanionic
ancillary ligand systems, the use thereof, and to the method of preparing and
20 using the same.

Background of the Invention

25

 Traditional Ziegler-Natta type catalysts for the polymerization of
olefins have been known since the 1950's. Generally, these catalysts comprise a
transition metal halide compound, particularly one of titanium and chloride,
and a metal alkyl cocatalyst, particularly an aluminum alkyl cocatalyst. The
traditional catalyst systems are generally comprised of several chemically
30 distinct active metal sites which produce different polymeric materials
(molecular weight comonomer, etc.) under steady state reactor conditions.
During the last 30 years of development, traditional Ziegler-Natta catalysts
have been optimized and provide low cost routes to a variety of commercially
important polyolefins, however further improvements over the control of key
35 polymer structure parameters such as molecular weight distribution (MWD),

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composition distribution (CD), end group functionality, sequence distribution and polar comonomer compatibility are still needed.

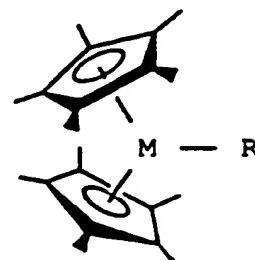
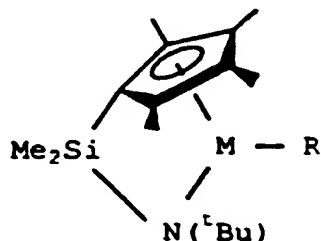
Recent progress to improve the Ziegler-Natta system has been directed towards the production of soluble, single sited olefin polymerization catalysts derived from transition metal precursors where the halide ligands used in tradition catalysts have been replaced by bulky, organic ancillary ligand systems, such as cyclopentadienyl (Cp) derivatives. In contrast to simple halide ligands, the bulky ancillary ligand systems are not susceptible to removal or change during polymerization, stabilize a single form of the catalyst, and can be modified in a rational way to change the properties of the catalyst center. The development of high activity catalyst systems derived from bis- and mono- Cp stabilized Group 4 metal precursors and alumoxanes is now well documented. Despite the fact that the cocatalyst (and therefore the resulting catalyst) is a chemically complex mixture of aluminum alkyl reagents, the active catalyst generally behaves as a single sited catalyst and produces narrow MWD polyolefins.

Recent advances in the art have led to the development of well defined (discrete), ancillary ligand stabilized single-sited olefin polymerization catalysts of the Group 3 and 4 transition metals. These systems do not rely on the use of alkyl aluminum cocatalysts, and offer improvements in terms of cost and product versatility. Examples of mono-Cp and bis Cp based Group 3 and 4 discrete catalysts are represented below.

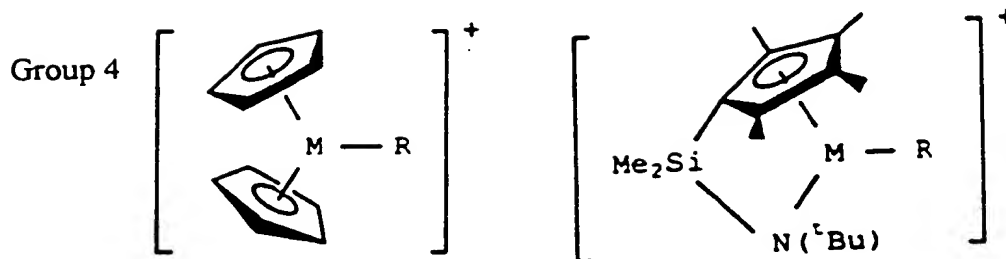
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Group 3



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The neutral Group 3 systems were prepared and studied by Ballard et al. (J. Chem. Soc., Chem. Comm., (1978) p. 994-995) and Bercaw et al. (Organometallics, Vol. 9 (1990) pp. 867-869). The work of Bercaw and others in this field has demonstrated that the neutral, three-coordinate systems tend to dimerize to form inactive four-coordinate systems when the size of the ancillary ligands is decreased. The use of bulky Cp ligands to sterically prevent self-dimerization and maintain catalytic activity has been successful, but the resulting systems are often too sterically hindered to allow for the incorporation of larger olefin monomers.

The discovery of isostructural and isoelectronic discrete mono- and bis-Cp based Group 4 cationic systems, are discussed in European Patent Application (EPA) 277,003 and EPA 277,004, PCT International Application WO 92/00333 and EPA 418,044. These cationic systems are stabilized by the ancillary ligand system and are isolated as the salts of specially designed compatible non-coordinating anions. The development of compatible non-coordinating anions, as disclosed in EPA 277,003 and 277,004 represents a major advance in the field because they provide a means by which highly reactive coordinatively unsaturated organometallic cations can be generated and isolated. Although the ionic Group 4 catalysts are greatly improved over the organoaluminum activated systems in terms of producing polymers having greater molecular weight, enhanced molecular weight distribution and composition distribution control, there exists a need to provide a catalyst with improved thermal stability, product versatility, and tolerance to polar functionality.

The need for improved single sited olefin polymerization catalysts is evident, particularly in terms of chemical stability (e.g., air stability) and

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tolerance to polar functionality. Improvements in these properties would yield catalysts which could tolerate greater levels of impurities in the monomer feeds, and which could incorporate polar comonomers into a polyolefin backbone. For this reason, it would be desirable to develop olefin
5 polymerization catalyst comprised of later transition metals. The best studied and well defined late metal catalysts for the polymerization of ethylene has been developed by Brookhart and coworkers (J. Am. Chem. Soc. 1985, 107, 1443-1444). These systems, $\text{Cp}^*\text{Co}(\text{L})\text{R}^+ \text{BX}_4^-$, are comprised of cationic cobalt (III) complexes containing a ligand, Cp^* , a neutral datively bound
10 ligand, L, and a reactive sigma-bound alkyl with the charge on the metal center balanced by a borate anion BX_4^- . While these catalyst systems offer some potential advantages, particularly with respect to compatibility with polar functionalities and for the production of very narrow molecular weight distributions, they suffer from very low activity and yield only a single polymer
15 chain per metal atom. A goal is to develop polymerization catalysts which combine the activity and yield of cationic Group 4 systems with the selectivity and functional group tolerance of later metal systems.

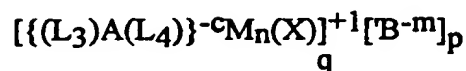
20 Summary of the Invention

This invention relates to Group 5-10 transition metal polymerization catalysts, wherein the transition metal is in a high oxidation state, stabilized by a low coordination number ancillary ligand system(s), the use thereof, and to
25 methods of preparing and using the same. The catalyst is an ion-pair comprised of a coordinatively unsaturated cationic transition metal complex having at least one reactive metal-ligand sigma bond and stabilized by a low coordination number polyanionic ancillary ligand system and charge balanced by compatible non-coordinating anions. The catalyst precursor, a neutral low
30 coordination number ancillary ligand containing transition metal complex, can be converted into the active ionic catalyst using Lewis acid activators such as methylalumoxane or $\text{B}(\text{C}_6\text{F}_5)_3$, or by ion-exchange reagents comprising a reactive cation and a compatible non-coordinating anion. The invention more particularly relates to compositions useful as olefin polymerization catalysts for
35 the production of polyolefins containing from 2 to 20 carbon atoms.

- 5 -

The preferred catalyst of this invention are ion-pairs comprising a cationic Group 5 or 6 transition metal complex defined by the following formula:

5



wherein:

10 M is a Group 5 or 6 transition metal in its highest formal oxidation state;

n is the Group number of the metal;

L₃ and L₄ are the same or different substituted or unsubstituted bulky anionic ancillary ligands covalently bonded to the metal;

15 A is an optional bridging group linking L₃ and L₄;

c represents the negative charge on the ancillary ligand system {L₃AL₄};

c + 2 = n.

20 X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals;

'B is a compatible non-coordinating anion of charge -m;

p is the number of 'B anions;

25 q is the number of +1 cations;

p times m = q; and



30 wherein:

M is group 5 or 6 transition metal in its highest oxidation state;

n is the group number of the metal;

L₃ and L₄ are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the metal;

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X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals;

A is an optional bridging group bridging L₃ and L₄;

5 c is an integer representing the charge on the ancillary ligand system {(L₃)A(L₄)};

$c + 2 = n$

B is a compatible non-coordinating anion of charge -m;

p is the number of B anions;

10 q is the number of +1 cations; and

p times m = q.

B is preferably a single anionic coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, which anion is bulky, labile and capable of stabilizing the transition metal compound.

15

B may be represented by the formula:

20 $M [Q_1 Q_2 \dots Q_n]^{d-}$

wherein:

M is a metal or metalloid;

Q₁ to Q_n are, independently, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals and any one, but not more than one of Q₁ to Q_n may be a halide radical;

25

n is the total number of Q ligands; and

30 d is an integer representing the total charge on the anion.

$\{(L_3)A(L_4)\}^c M_n X_2$

wherein:

35 M is a Group 5 or 6 transition metal in its highest oxidation state (d⁰);

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L_3 and L_4 are bulky, ancillary anionic ligands such that the sum of their formal anionic charge is equal to c ;

$$c + 2 = n;$$

X is independently a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals;

A is an optional bridging group linking L_3 and L_4 ; and,

n is the group number of the metal;

with

(ii) a second component comprising an ion-exchange compound comprising a cation, which will irreversibly react with at least one ligand, X , contained in said Group 5 or 6 metal compound and a compatible non-coordinating anion;

with

an ionizing activator component which may be an ion-exchange compound comprising a cation, which will irreversibly react with at least one ligand, X , contained in said Group 5 or 6 metal compound and a non-coordinating anion. Alternatively, the transition metal compound may be reacted with a Lewis acid capable of abstracting the ligand X to form a compatible non-coordinating anion.

The compositions described may be placed on a support and optionally prepolymerized prior to use as a catalyst for olefin polymerization.

25

Detailed Description of the Invention:

Key features of known single-sited olefin polymerization catalysts include a coordinatively unsaturated, electrophilic metal center in a trigonal environment, an active sigma bound substituent, preferably an alkyl, and at least a single vacant orbital adjacent (cis) to the sigma bound ligand. A set of inert ancillary ligands are present in these systems to establish and maintain the proper electronic and steric environment of the metal center throughout the polymerization. Ancillary ligands may be defined as ligands which do not participate in the polymerization but which are covalently bonded to the metal by single or multiple bonds. Ancillary ligands are typically composed of

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organic and/or inorganic moieties in a discrete and well defined manner and preferably have a molecular weight about or greater than 50 amu (atomic mass unit). A prototypical example of an ancillary ligand is the Cp group. Neutral complexes containing the features of olefin polymerization catalysts defined
5 above are unstable with respect to self dimerization unless very large ancillary ligands are present. Charged metal complexes meeting the above defined criteria of polymerization catalysts do not require bulky ancillary ligands to prevent self-dimerization. The use of electrostatic rather than steric forces to control dimerization allows for much greater reactivity of these ionic species
10 with larger olefinic substrates.

The electronic nature of the metal centers in these systems is critical in determining the ultimate reactivity of the catalyst. For early transition metal systems, complexes of the highest possible formal oxidation state (d^0 complexes) are preferred. In late metal systems such as Brookhart's cobalt
15 complexes, the highest formal oxidation states are inaccessible. In these systems, the highest oxidation state which is accessible is desirable. Residual electron density at the metal center of these systems renders them more tolerant to polar functionality, but diminishes the rate of chain propagation relative to that of chain termination, and in some instances this results in low
20 molecular weight polymers. The formation of high molecular weight polymer in these systems demands a careful balancing of the electron density at the metal center.

The challenge of capturing unique features of metal systems later than Group 4 lies in constructing higher oxidation state complexes which remain
25 coordinatively unsaturated. This invention relates to the design and use of ligand systems based on low coordination number polyanionic ligands for the construction of olefin polymerization catalysts based transition metals of groups greater than Group 4. Low coordination-number polyanionic ancillary ligands (LCPALs) are defined as ancillary ligands which have a greater formal
30 negative charge than the number of sites they occupy. As a system, these ligands possess the unique property of oxidizing the metal center to a greater extent than they fill occupation sites on that metal and thus provide a method of maintaining high oxidation states and low coordination numbers.

The single-sited olefin polymerization catalysts of this invention are
35 comprised of a coordinatively unsaturated cationic transition metal complex

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from the Groups 5-10 of the Periodic Table having (Grant & Hackh's Chemical Dictionary 5th ed. 1987, p. 433.) at least one reactive metal - ligand sigma bond and stabilized by a low coordination number polyanionic ancillary ligand system. The ancillary ligand system is designed to stabilize the metal in a high oxidation state using a minimum number of coordination sites (preferably 2). Illustrative but not limiting examples of polyanionic ligands which can be used in this invention include bulky imides such as t-butylimido and 2,6-diisopropylimido, and carbolides such as $C_2B_9H_{11}^{2-}$ and $CB_{10}H_{11}^{3-}$. The polyanionic ligands can be used alone, or in combination with conventional monoanionic ancillary ligands (such as Cp derivatives, alkoxides, aryloxides, amides phosphides, and the like) or neutral ancillary ligands (such as phosphines, amines, carbonyls and the like) to form an ancillary ligand system. Two ancillary ligands systems may be optionally bridged together through a bridging group, A. In addition, the cationic transition metal complex may be stabilized by a displaceable Lewis base ligand. The cationic transition metal complex is charge balanced by compatible non-coordinating anions which are weakly coordinated to the active metal center thereby being sufficiently labile to be displaced by a neutral Lewis base such as an olefin. As recited herein the term "compatible non-coordinating anion" specifically refers to anions which are bulky relative to the size of the vacant coordination site and which are resistant to chemical reactions with the active metal center, such as transfer of a negatively charged fragment to the cation to form neutral biproducts. Illustrative but not limiting examples of cations of this invention include d⁰ Group 5 systems such as $(C_5Me_5)(C_2B_9H_{11})TaCH_3^+$, wherein Me is methyl, and $(C_5Me_5)(RN)TaCH_3^+$ (where R = alkyl or aryl); d⁰ Group 6 systems such as $(C_2B_9H_{11})_2WCH_3^+$ and $(RN)_2WMe^+$; d⁰ Group 7 systems such as $(C_2B_9H_{11})(CB_{10}H_{11})ReMe^+$, d⁰ Group 8 systems such as $(CB_{10}H_{11})_2OsMe^+$, and d⁶ Group 10 systems such as $(C_2B_9H_{11})(Ph_3P)NiCH_3^+$ where Ph is phenyl, and Lewis base adducts thereof.

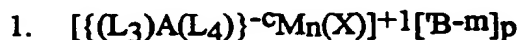
The active catalysts of this invention can be prepared from a neutral transition metal precursor comprising the polyanionic ligand system using a variety of activating strategies. One general strategy for forming the active catalyst involves reacting the neutral precursor with an ion-exchange compound comprising a cation capable of removing a negatively charged

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ligand (or electron) from the neutral transition metal precursor and a compatible non-coordinating anion. Another approach involves the use of discrete Lewis acid coactivators such as $B(C_6F_5)_3$ with the neutral transition metal precursor to remove an anionic non-ancillary ligand from the transition metal precursor to form the active catalyst cation and a non-coordinating anion comprised of the Lewis acid coordinated to the anionic non-ancillary ligand. In general, active catalysts can also be generated using alumoxanes, preferably methylalumoxane in combination with the neutral transition metal precursor. A more detailed description of these approaches is given below.

Preferred Embodiments

The preferred catalysts of this invention are Group 5 and 6 transition metal catalysts having the following general structural features: 1) two ancillary stabilizing ligands; 2) one reactive sigma metal-ligand bond such as a metal carbon or hydride bond; 3) the metal center in its highest formal oxidation state (d0); and 4) a total formal charge of +1 on the transition-metal center. The preferred catalysts comprise the ion pair represented by the formula:



wherein:

M is group 5 or 6 transition metal in its highest oxidation state;

n is the group number of the metal;

L_3 and L_4 are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the metal;

X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals;

A is an optional bridging group bridging L_3 and L_4 ;

c is an integer representing the charge on the ancillary ligand system $\{ (L_3)A(L_4) \}$;

$$c + 2 = n$$

B is a compatible non-coordinating anion of charge -m;

p is the number of B anions;

q is the number of +1 cations; and

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p times m = q.

The list optional X-ligands given in the above formula are the preferred selections. Other X-ligand options are also suitable for catalysts of this invention, for example, any X-group which forms a single metal-ligand sigma bonds with little or no pi or multiple bond character. Thus, metal complexes containing metal X-ligands other than those listed in the formula above that are bonded to the metal through a single sigma bond with no multiple bond character are operable and included in this invention.

The ancillary ligand system comprised of $\{L_3-A-L_4\}$ is a low coordination number polyanionic ligand system for which the total anionic charge of $\{L_3-A-L_4\}$ is greater than the number of coordination sites it occupies. Those of ordinary skill in the art will recognize that for unbridged ancillary ligands, Group 5 catalysts will be comprised of one dianionic LCPAL, one uninegative ancillary ligand, and one uninegative ligand X, defined above. Similarly, Group 6 metal catalysts will be comprised of two dianionic LCPALs and one uninegative ligand X, or one trianionic LCPAL, one uninegative ancillary ligand, and one uninegative ligand X. The bridging of ligands L_3 and L_4 with neutral, non-coordinating, bridging groups A results in the formation of a single ligand for which the charge and coordination number are the sum of those for L_3 and L_4 . The use of anionic, non-coordinating, bridging groups A allows for the construction of LCPALs from uninegative ancillary ligands which are well known in the art.

Illustrative but not limiting examples of ancillary ligands from which to chose a ligand set meeting the above criteria include: uninegative ancillary ligands well known to those of skill in the art such as substituted or unsubstituted Cp moieties, amides such as bis-trimethylsilylamido, bis-t-butylamides, bulky alkoxides such as tri-t-butylalkoxide; dianionic LCPALs such as oxo ($=O$), sulfido ($=S$), imido ($=NR$), phosphido ($=PR$), alkylidenes ($=CR_2$), cyclooctatetraenyl ($[C_8H_8-xR_x]^{2-}$), porphyrins, phthalocyanines, corrins, and other anionic polyazamacrocycles; carbollides (e.g. $[C_2B_9H_{11}]^{2-}$), bis(o-hydroxyphenyl)alkyl and -arylphosphine oxides ($(h^3-(RPO(C_6H_4O)_2)^{2-})$); and borollides; and trianionic LCPALs such as nitrido ligand ($=N$), alkylidyne ($=CR$), trianionic carbollides (e.g. $[CB_{10}H_{11}]^{3-}$) and trianionic corroles.

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Examples of LCPALs comprised of anionic bridging groups include $[\text{Cp-B(Ph)}_2\text{-Cp'}]^{3-}$ where Cp and Cp' are substituted or unsubstituted cyclopentadienyl ligands. Higher valent LCPALs are known to bond to transition metals and can be used in this invention. The ancillary ligands and optional bridging groups on the first components of this invention may be substituted with a wide range of substituent types without rendering them inoperative as catalyst precursors. For example, all of the suitable substituents for catalyst precursors in the patent applications incorporated herein by reference may be used to modify the ancillary ligands and bridging groups of the first components and catalysts of this invention. These substituents may further be modified with any functionality which is not itself a catalyst poison. Furthermore, the size, as measured by molecular weight, of the substituent may be varied over a wide range without effecting the operability of the precursor or catalyst and thus are included in this invention.

15

The borollide ligands are illustrated in general formula:



20 wherein:

B is boron;

C is carbon;

each R and R' is, independently, a hydrocarbyl radical, substituted-hydrocarbyl radical, halocarbyl radical, substituted-halocarbyl radical, hydrocarbyl-substituted organometalloid radical, halocarbyl-substituted organometalloid radical, disubstituted Group 15 radical, substituted Group 16, or halogen radical; any two adjacent R groups or adjacent R and R' groups can be joined to form a cyclic substituent; and x is 0, 1, 2, 3, or 4.

30

Known methods of preparing borollide dianions, such as disclosed by G.E. Herberich, Comprehensive Organometallic Chemistry Pergamon Oxford, Vol. 1, p. 381-410 (1984), include the reduction of neutral borole precursors by alkali metals or their amalgams, reduction of neutral borole precursors within the coordination sphere of the low-valent transition metal complex, and deprotonation of 1-(dialkylamino)-2,5-dihydroboroles.

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Illustrative, but not limiting, examples of suitable bridging groups A include: C₁-C_n saturated or unsaturated hydrocarbyl diradicals, substituted or unsubstituted carbenoids R₂C, hydrocarbyl substituted silyl, germyl, or stanyl groups; and dialkyl and diaryl borates.

Examples of compatible non-coordinating anions include but are not limited to boranes, polynuclear boranes, carboranes, metallacarboranes, polyoxoanions, and anionic coordination complexes are well described in the literature (see EPA 277,003, EPA 277,004, EPA 520732 which are herein incorporated by reference). US Patent No. 5,198,401 incorporated by reference herein, describes compatible non-coordinating anions, and anionic coordination complexes, and teaches to design superior counter anions. Preferred non-coordinating anions comprise a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, which anion is bulky, labile and capable of stabilizing the transition metal cation. Anionic coordination complexes may be represented by the following formula:



wherein:

M is a metal or metalloid;

Q₁ to Q_n are, independently, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals and any one, but not more than one of Q₁ to Q_n may be a halide radical;

n is the total number of Q ligands; and

d is an integer representing the total charge on the anion.

The most preferred compatible non-coordinating anions comprise at least three perfluorophenyl groups coordinated to boron and are represented by the formula B(pfp)₃Q₁⁻ (where pfp = C₆F₅).

The catalyst composition defined in equation (1) can react with Lewis base ligands which may be present as biproducts of the first component synthesis or which may be added in catalyst to form coordination complexes of

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(1). The resulting coordination complex will generally be an active catalyst for olefin polymerization, however, the activity and or performance of the catalyst may be modified by the choice of Lewis base.

5 The Group 5 or 6 transition metal catalyst described may be employed in solution, slurry, bulk-phase, high pressure or gas-phase polymerization processes, or a combination thereof, to produce a polyolefin of high molecular weight, high comonomer content, and/or narrow molecular weight distribution.

Catalyst Preparation

10 The catalysts are preferably prepared by combining at least two components, the Group 5 or 6 transition-metal-containing component (first component) containing at least one ligand capable of reacting with a second, ionizing activator component (second component). The transition-metal component, or catalyst precursor, is comprised of the first component
15 represented by the following formula:



wherein:

20 M is a Group 5 or 6 transition metal in its highest oxidation state (d0);
L₃ and L₄ are bulky, ancillary anionic ligands such that the sum of their formal anionic charge is equal to c;

$$c + 2 = n;$$

25 X is independently a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals;

A is an optional bridging group linking L₃ and L₄; and,

n is the group number of the metal;

30 with

(ii) a second component comprising an ion-exchange compound comprising a cation, which will irreversibly react with at least one ligand, X, contained in said Group 5 or 6 metal compound and a compatible non-coordinating anion.

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The preparation of first components having the structure defined in equation 4 depends upon the choice of L_3 and L_4 . In general, synthetic strategies for preparing transition metal complexes comprising the mono- and poly-valent ancillary ligands of this invention are known in the art and can be applied to the synthesis of the desired first component. In a typical preparation the lithium salts of L_3 , L_4 , or L_3AL_4 are combined in an organic solvent with the metal halide in its highest oxidation state. Other conventional salts such as Group 1 salts or Grignards of Group 2 salts may be employed. In some cases, such as when imide is used, the lithium salt approach may not ideal and standard "imide" transfer reactions can be used. Generally the ancillary ligands of this invention may be prepared in accordance with known procedures.

Second components useful for converting the transition metal precursor (4) into the catalytically active ion-pair (1) are either an ion exchange reagent as defined in equation (5) or a well defined Lewis acid defined in equation (6) below:



wherein:

M is a metal or metalloid;

Q_1 to Q_n are, independently, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals and any one, but not more than one of Q_1 to Q_n may be a halide radical;

n is the total number of Q ligands; and

d is an integer representing the total charge on the anion.

Ct is a cation reactive the X -ligand or electron of the first component.



wherein:

M' is a metal or metalloid in its highest oxidation state;

r represents the number of Q ligands;

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and Q is selected from the group consisting of hydride radicals, dialkylamido radicals, alkoxide and alkoxide radicals, hydrocarbyl and substituted hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals, and hydrocarbyl- and halocaryl-substituted organometalloid radicals. M' is preferably boron and Q is preferably C₆F₅.

Upon combination of the first and second components, the second component, or at least a portion thereof, reacts with one of the ligands of the first component, thereby generating an ion pair consisting of a transition-metal cation and the aforementioned anion, 'B, which anion is compatible with the transition-metal cation formed from the first component. The anion must generally be capable of stabilizing the transition-metal cations ability to function as a catalyst and must generally be non-coordinating or sufficiently labile to permit displacement by an olefin, diolefin, or acetylenically unsaturated monomer during polymerization.

Catalyst precursors represented by equation 4 may be converted to the active catalysts represented in equation 1 by several routes depending on the nature of the precursors and ligands X. A list of illustrative, but not limiting examples of such methods are disclosed below.

The first method involves contacting the first component (4) with a second component [Ct]_m['B]^{m-} where the cation Ct is an oxidizing agent which is reduced during the formation of the ion pair of equation 1. Examples of preferred second components for this application include [Cp'₂Fe]⁺['B]⁻ and Ag⁺['B]⁻ (where 'B is B(pfp)₃Q₁ as defined above). For less reactive first components more highly oxidating cations may be employed. This approach is useful with first components with low oxidation potentials.

A second method uses Bronsted acid salts of compatible non-coordinating anions as the second component having the following general formula:



wherein:

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[LH] is a Bronsted Acid of charge +1

L is a neutral Lewis base;

'B is a compatible non-coordinating anion; and

m represents the charge of 'B and the number of [LH]

5 cations.

When the two components are combined in a suitable solvent (aliphatic or aromatic solvents are preferred) the acidic proton of the cation reacts with one of the X-ligands of the first component to liberate a non-reactive neutral product (X-H), a neutral Lewis base L, which may remain in solution or
10 weakly bind to the metal cation, and the composition defined by equation 1. This approach is generally useful for first components having X-ligands which are hydrolyzable by water. Bronsted acid salts having acidic protons are preferred for first components which are resistant to degradation by water. Examples of Bronsted acid cations useful as cations of the second component
15 include ammonium ions (R_3NH^+), phosphonium ions (R_3PH^+), and oxonium ions (R_2OH^+).

A third method involves reacting Lewis acid salts of compatible non-coordinating anions catalyst precursors with the first components of equation
20 4. Examples of Lewis acidic cations useful as cations of the second component include reactive transition metal cations such as $[Cp_2MMe(NR_3)]^+$ (where M = a Group 4 metal), reactive carbonium ions such as $[CPh_3]^+$ and tropylium, and organometallic main group cations such as $[ZnMe]^+$.

25

A fourth approach involves reacting well defined neutral Lewis acid second components with first components defined by equation 4. The neutral Lewis acid second components are generally defined by equation 6. The preferred Lewis acid is $B(pfp)_3$. The neutral Lewis acid removes a negatively
30 charged X-ligand from the first component to form the active transition metal cation and the compatible non-coordinating anion (e.g. when $B(pfp)_3$ is used the non-coordinating anion is $B(pfp)_3X^-$). In general, increasing the Lewis acidity of the second component by introducing electron withdrawing groups on the ligand system will lead to more powerful coactivators capable of
35 activating a wider variety of first components.

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Other approaches for the production of catalysts of this invention which do not rely on the first component defined by equation 4 include the two general procedures listed below.

5

The first method involves reacting a second component comprising an oxidizing cation with the first component defined below:



10

wherein the symbols are defined in equation 4 except there is only one X-ligand and the metal is in the n-1 oxidation state (d^1). Examples of preferred second components for this application include $[Cp'_2Fe]^+[B]^-$, $Ag^+[B]^-$ (where B is $B(pfp)_3Q_1$ as defined above).

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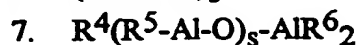
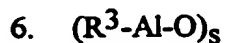
Another general method involves adding one or more of the stabilizing ancillary ligands to the metal center subsequent to the formation of the cationic center. For example, the reaction of equimolar amounts of $C_2B_9H_{13}$ and $[Cp^*TaMe_3]^+[B]^-$ could lead to the formation of $[Cp^*(C_2B_9H_{11})TaMe]^+[B]^-$ wherein Cp^* can be a substituted or

20

unsubstituted Cp group.

Yet another general method of activating the first components of equation 4 involves the use of hydrolyzed Lewis acids defined by the following general formulae:

25



30

It will apparent to those of skill in the art that a wider variety of X groups on the first component may be used when alumoxanes are the cocatalyst. These include halides, alkoxides, amides, phosphides and the like.

35

In the general formulae 6 and 7, representing alumoxane or a derivate thereof, Al is aluminum, O is oxygen, R^3 , R^4 , R^5 and R^6 are, independently a C_1 - C_6 alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "s" is an integer from 1 to 50. Most preferably, R^3 , R^4 , R^5 and R^6 are, each

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methyl and "s" is at least 4. When an alkyl aluminum halide is employed in the preparation of the alumoxane, one or more R^{3-6} groups may be halide.

5 As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane.

10 Suitable alumoxanes which may be used in the catalysts of this invention are those prepared by the hydrolysis of a trialkylaluminum, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, dimethylaluminum chloride, diisobutylaluminum chloride, diethylaluminum chloride. The most preferred alumoxane for use is methylalumoxane (MAO).
15 Methylalumoxanes having an average degree of oligomerization of from 4 to 25 ("s" = 4 to 25), with a range of 13 to 25 are the most preferred and employed in a mole ratio of MAO to transition-metal component of 1:1 to 106:1.

20 In general, the catalyst of this invention can be prepared by combining the first and second components in a suitable solvent or diluent at a temperature within the range of -100°C to 300°C . The catalyst may be used to polymerize olefins, including cyclic olefins, alpha-olefins, diolefins, and/or acetylenically-unsaturated monomers having 2 or more carbons atoms, either
25 alone or in combination with other monomers or monomer mixtures. In general, the polymerization can be accomplished at conditions known in the art. It will, of course be appreciated that the catalyst will form in situ if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said
30 polymerization process. It is, however, preferred to form the catalyst in a separate step in a suitable solvent or diluent prior to adding the same to the polymerization step. Preferred temperatures for the reaction of the two components are from -30°C to 100°C , with holding times from 15 seconds to 60 minutes. The catalyst may contain pyrophoric species, especially

- 20 -

methylalumoxane, and should be handled and transferred in an inert atmosphere such as nitrogen, argon, or helium.

As indicated above, the improved catalyst of this invention will, preferably, be prepared in a suitable solvent or diluent. Suitable solvents or diluents include any of the solvents known in the prior art to be useful in the polymerization of monomers. Suitable solvents, then, include, but are not limited to, straight- and branched-chain aliphatic hydrocarbons such as isobutane, butane, hexane, heptane, octane; cyclic and alicyclic aliphatic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane; and aromatic and alkyl-substituted aromatic solvents such as benzene, toluene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 1,4-hexadiene.

15

In order to achieve greater control of polymer particle size and distribution and compatibility with gas-phase polymerization processes, the catalysts may be supported on appropriate inert materials, as described in US Patent Nos. 4,701,432, 5,006,500, 5,008,228, and as described in PCT International Application WO 91/09882. The supported catalysts may be optionally prepolymerized with olefinic monomers.

20

Having thus broadly described the present invention and preferred embodiments thereof, it is believed that the same will become even more apparent by reference to the following examples. It will be appreciated, however, that the examples are presented solely for the purpose of illustration and should not be construed as limiting the invention. All the examples were carried out in dry, oxygen-free atmospheres and solvents, molecular weights are reported as weight average molecular weights, MAO was purchased from Schering Company, Dublin Ohio.

25

30

Example 1

First Component Synthesis: In an inert atmosphere, vanadium oxide trichloride (2.75 g) was dissolved in dichloromethane (100 ml) and potassium tris(pyrazolyl)borate (2.0 g) added slowly. The mixture, which turned from

35

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dark orange to purple, was stirred overnight. The volatiles were removed in vacuo. A 70:30 pentane/dichloromethane mixture was added and the solids were collected, washed with pentane until no color was observed in the washings, and dried. Yield: 3.28 g. The ^1H NMR spectrum (CD_2Cl_2) of the solid showed this to be a diamagnetic solid, tris(pyrazolyl)borato vanadium oxide dichloride. A 1 gram sample was dissolved in boiling toluene (60 ml), filtered, and the filtrate reduced in vacuo. Crystallization from dichloromethane-pentane yielded 0.45 g of product.

Ethylene Polymerization: To a 1 liter stainless-steel autoclave, previously purged with nitrogen, was added 5 ml of a 9.5 weight percent solution of methylalumoxane in toluene. 400 ml of dry, deoxygenated hexane were then added, followed by a solution of the catalyst of Example 1 (30 mg) in toluene (5 ml). The contents of the autoclave were stirred, heated to 60°C , and pressurized with ethylene (200 psi) (13.6 atm). After 30 minutes, the autoclave was cooled and vented. The polyethylene formed was isolated by filtration and dried. Yield: 16 g.

Example 2

Ethylene Polymerization: Ethylene was polymerized in a manner similar to that of Example 1 using (cyclopentadienyl)vanadium (p-tolylimido) dichloride, prepared by the method reported by Maatta et al., (Journal of the American Chemical Society, Volume 109 (1987), pp. 7408-7416) as the metal component. The yield of linear polyethylene was 5.8 g.

Example 3

Catalysis Synthesis: preparation of $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{TaMe}_2$ (where $\text{Me} = \text{CH}_3$, and $\text{Cp}^* = \text{C}_5\text{Me}_5$): Cp^*TaMe_4 (1.0 g, 2.6 mmol, prepared by known literature procedures) and $\text{C}_2\text{B}_9\text{H}_{13}$ (0.36 g, 2.6 mmol, prepared by the known literature methods) were combined and stirred at room temperature in toluene for 30 minutes. The solvent was removed in vacuo to leave a solid yellow product. The crude product was extracted with toluene, filtered, concentrated to the point of crystallization. The yellow crystalline product was isolated by filtration and dried in vacuo to yield 0.4 grams of $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{TaMe}_2$ (as characterized by NMR spectroscopy).

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Ethylene polymerization: A stainless steel autoclave reactor was charged with hexane (400 cc), $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{TaMe}_2$ (10 mg) and methylalumoxane (5 ml, 1.6M). The reactor was heated to 40°C and
5 pressurized with 200 psig (13.6 atm) (14 bar) of ethylene. The reactor was stirred for 30 minutes and vented. This procedure produced 1.5 grams of high molecular weight polyethylene.

Example 4

10 Catalysis Synthesis: Synthesis of $(\text{C}_2\text{B}_9\text{H}_{11})\text{W}=\text{NAr}(\text{Me})(\text{Cl})$: The starting material, $\text{W}=\text{NAr}(\text{Me})_3\text{Cl}$ (Ar = 2,6-dimethylbenzene), was prepared by known literature methods. A mixture of $\text{W}=\text{NAr}(\text{Me})_3\text{Cl}$ (1.8 g, 5 mmol) and $(\text{C}_2\text{B}_9\text{H}_{13})$ (0.7 g, 5 mmol) in 30 ml of toluene was heated to 65°C under
15 an N_2 atmosphere. After 48 hours, the toluene was removed under reduced pressure to yield an oily red residue. The crude product was washed with pentane and filtered over a glass frit to yield a dark red solid (Yield: 1.2 g, 53%).

Ethylene Polymerization: The catalyst solution was prepared
20 immediately before use. A solution of 30 mg $(\text{C}_2\text{B}_9\text{H}_{11})\text{W}=\text{NAr}(\text{Me})(\text{Cl})(\text{Et}_2\text{O})$ and 3.0 ml, 10% MAO in toluene solution was diluted to 10 ml with toluene. Polymerization was performed in a one liter autoclave reactor at 150-200 psi (10.2-13.6 atm) (14 bar) and 40-50°C with 250 ml toluene. The reactor was vented after 25 min. The yield of
25 linear PE was 6.7 g with $\text{Mw} = 1.1 \times 10^6$ and a polydispersity of 1.8. The catalyst activity was calculated to be 536 g PE/g W.hr.

Example 5

Ethylene Polymerization: A catalyst solution containing
30 $(\text{C}_2\text{B}_9\text{H}_{11})\text{W}=\text{NAr}(\text{Me})(\text{Cl})$ (50 mg) prepared in accordance with Example 4 and 5.0 ml 10% MAO in toluene was diluted to 15 ml with toluene. The solution was added in 2.0 or 3.0 ml increments during the initial 5 minutes of polymerization to an ethylene-saturated solution of toluene (500 ml) at 80°C. The initial pressure was 200 psi (13.6 atm) (14 bar) and was increased to 300
35 psi (20.4 atm) and the temperature was increased to 90°C. After allowing

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polymerization to occur for 25 minutes, the reactor was cooled and vented. A yield of 9.8 g polyethylene was obtained with $M_w = 5.6 \times 10^5$ and polydispersity of 2.1.

5 Example 6

Propylene Polymerization: A bulk polymerization was performed at 370 psi (25.2 atm) (26 bar) with 80 ml toluene. 3.0 ml of 10% MAO in toluene was loaded into the autoclave reactor initially to act as a scavenger followed by a solution of 28 mg ($C_2B_9H_{11}$) $W=NAr(Me)(Cl)$ prepared in accordance with
10 Example 4 in 1 ml toluene. A temperature of 40°C was maintained for the duration of the reaction time totaling 40 minutes. A yield of 1.5 g of polypropylene was obtained with $M_w = 2 \times 10^4$ and a polydispersity of 5.2.

Example 7

15 Catalysis Synthesis: Preparation of $W(=NAr)_2(CH_2SiMe_3)_2$ wherein Ar is 2,6-diisopropylbenzene. $W(=NAr)_2Cl_2$ was prepared by known literature methods. A solution of 0.40 g $W(=NAr)_2Cl_2$ (.70 mmol) in 20 ml Et_2O was cooled to -35°C. Slowly, 0.70 ml 1.0 M Me_3SiCH_2MgCl in Et_2O was syringed into the cooled solution and the reaction mixture was allowed to
20 stir for 17 hours while warming to room temperature. The Et_2O was removed in vacuo, the crude orange solid extracted with pentane, and the extracts filtered through Celite. After removing the pentane in vacuo, 0.25 g orange $W(=NAr)_2(CH_2SiMe_3)_2$ was obtained (Yield: 47%).

25 Ethylene Polymerization: Toluene (500ml) was saturated with ethylene under a pressure of 200 psi (14 bar, 13.6 atm) at 80°C in a one liter autoclave reactor. A catalyst solution of 42 mg of $W(=NiPAr)_2(CH_2SiMe_3)_2$ and 5.0 ml 10% MAO in toluene was loaded into the reactor in two 2.5 ml increments during the first 5 minutes of polymerization. The polymerization was allowed
30 to proceed for a total of 25 minutes. The temperature was maintained at a constant 80°C and the pressure from 200 to 250 psi (13.6 to 17 atm) (14-17 bar). The amount of dried polymer obtained was 10.1 g, giving a catalyst activity of 721 g PE/g W·hr.

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Example 8

Catalysis Synthesis: $\text{CpNb}=\text{N}(2,6\text{-diisopropylbenzene})\text{Me}_2$ was prepared by the reaction of MeMgI with $\text{CpNb}=\text{N}(2,6\text{-diisopropylbenzene})\text{Cl}_2$ in diethylether at room temperature. The dichloride was prepared by known
5 literature methods.

Ethylene Polymerization: The catalyst solution was prepared immediately before use. A solution of 80 mg $\text{CpNb}=\text{N}(2,6\text{-diisopropylbenzene})\text{Me}_2$ and 89 mg $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ was prepared in 20ml toluene. Polymerization
10 was performed in a one liter autoclave reactor at 150-200 psi and 40-50°C with 500 ml hexane. The reactor was vented after 20 min. PE (as determined by ^1H NMR) was separated from the reaction mixture (Yield: 250 mg).

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CLAIMS

1. A composition of matter useful as an olefin polymerization catalyst comprising a coordinatively unsaturated cationic transition metal complex having at least one reactive metal-ligand sigma bond, said cation stabilized by a low coordination number polyanionic ancillary ligand system and charge balanced with at least one compatible non-coordinating anion(s).

2. The composition of claim 1 wherein the metal is one of the Groups 5 and 6 transition metals in its highest oxidation state (d^0).

3. A composition of matter comprising this ion-pair represented by the following formula:



wherein:

M is group 5 or 6 transition metal in its highest oxidation state;

n is the group number of the metal;

L_3 and L_4 are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the metal;

X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals;

A is an optional bridging group bridging L_3 and L_4 ;

c is an integer representing the charge on the ancillary ligand system

$\{(L_3)A(L_4)\}$;

$c + 2 = n$

B is a compatible non-coordinating anion of charge -m;

p is the number of B anions;

q is the number of +1 cations; and

p times m = q.

4. The composition of claim 3 where in 1 to 3 Lewis base ligands are coordinated to the metal cation.

5. The composition of claim 3 wherein B, is a single anionic coordination complex comprising a plurality of lipophilic radicals covalently coordinated to

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and shielding a central charge-bearing metal or metalloid atom, which anion is bulky, labile and capable of stabilizing the transition metal compound.

6. The composition of claim 5 wherein 'B is represented by:



wherein:

M is a metal or metalloid;

10 Q_1 to Q_n are, independently, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals and any one, but not more than one of Q_1 to Q_n may be a halide radical;

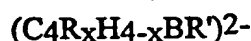
n is the total number of Q ligands; and

d is an integer representing the total charge on the anion.

15

7. The composition of claim 6 wherein 'B is $B(pfp)_3Q_1$ wherein B is boron, Q_1 is in accordance with Claim 5, and pfp is pentafluorophenyl.

20 8. The composition of claim 3 wherein L_3 and/or L_4 are represented by the formula:



wherein:

25 B is boron;

C is carbon;

each R and R' is, independently, a hydrocarbyl radical, substituted-hydrocarbyl radical, halocarbyl radical, substituted-halocarbyl radical, hydrocarbyl-substituted organometalloid radical, halocarbyl-substituted organometalloid radical, disubstituted Group 15 radical, substituted Group 16, 30 or halogen radical; any two adjacent R groups or adjacent R and R' groups can be joined to form a cyclic substituent; and x is 0,1,2,3, or 4.

35 9. The composition of claim 3 wherein the ligand system $\{(L_3)A(L_4)\}$ comprises at least one polyanionic ancillary ligand.

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10. The composition of claim 9 wherein the polyanionic ancillary ligand set is selected from the same or different borollide, carbollide, or imido ligands.

- 5 11. A process for the preparation of the composition of claim 3 comprising reacting a first component comprising:



10 wherein:

M is a Group 5 or 6 transition metal in its highest oxidation state (d0);

L₃ and L₄ are bulky, ancillary anionic ligands such that the sum of their formal anionic charge is equal to c;

$$c + 2 = n;$$

- 15 X is independently a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals;

A is an optional bridging group linking L₃ and L₄; and,

20 n is the group number of the metal;

with

- (ii) a second component comprising an ion-exchange compound comprising a cation, which will irreversibly react with at least one ligand, X, contained in said Group 5 or 6 metal compound and a compatible non-coordinating anion.
- 25

12. The process of claim 11 wherein the ion-exchange compound is represented by the formula:



30 wherein

Ct⁺ is selected from Bronsted acids, ferricinium cation, tropylium cation, Ph₃C⁺, and Ag⁺;

m is the charge on B; and

B is a compatible non-coordinating anion.

35

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13. The process of claim 12 wherein Ct^+ is a Bronsted acid defined by LH^+ where L is a neutral Lewis base and H is a hydrogen atom.

14. The process of claim 12 wherein 'B' is selected from anionic boranes, polynuclear boranes, carboranes, metallacarboranes, polyoxoanions, and anionic coordination complexes.

15. The process of claim 12 wherein 'B' is represented by the formula:



10 wherein:

M is a metal or metalloid;

15 Q_1 to Q_n are, independently, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals and any one, but not more than one of Q_1 to Q_n may be a halide radical;

n is the total number of Q ligands; and

d is an integer representing the total charge on the anion.

20 16. The process of claim 15 wherein 'B' is $B(pfp)_3Q_1$ where B is boron; and pfp is perfluorophenyl.

17. The process of claim 11 wherein the ligand system $\{(L_3)A(L_4)\}$ comprises at least one polyanionic ancillary ligand selected borollide, carbollide, or imido ligands.

18. The process for the preparation of the composition of claim 3 comprising the reaction of a transition metal precursor composition; wherein $\{(L_3)(L_4)\}^{-c}(A)M_nX_2$ is combined with a Lewis acid said Lewis acid capable of abstracting the ligand X.

19. The process of Claim 18 where the Lewis acid is defined by the following formula:



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wherein:

M' is a metal or metalloid in its highest oxidation state;

r represents the number of Q ligands;

and Q is selected from the group consisting of hydride radicals,
 5 dialkylamido radicals, alkoxide and alkoxide radicals, hydrocarbyl and
 substituted hydrocarbyl radicals, halocarbyl and substituted halocarbyl radicals,
 and hydrocarbyl- and halocaryl-substituted organometalloid radicals.

20. The process of claim 19 wherein the Lewis acid is
 10 tris(pentafluorophenyl)boron.

21. The process of preparing the compositions of Claim 3 comprising reacting
 a first component comprising the metal complex represent by:

15 (i) $\{(L_3)A(L_4)\}^{-c}M_nX$

wherein:

M is a Group 5 or 6 transition metal in the n-1 oxidation state (d1);

n is the group number of the metal;

20 L_3 and L_4 are ancillary anionic ligands such that the sum of their
 formal anionic charge is equal to c;

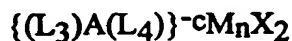
$c + 2 = n$;

X is independently a uninegative ligand selected from hydride radicals,
 hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl
 25 radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-
 substituted organometalloid radicals; and,

A is an optional bridging group bridging L_3 and L_4 ;

with a second component comprising a cation capable of oxidizing M to the +n
 30 oxidation state and a compatible non-coordinating anion.

22. A composition of matter comprising the reaction product comprising:



35 wherein:

- 30 -

M is group 5 or 6 transition metal in its highest oxidation state;

n is the group number of the metal;

L₃ and L₄ are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the metal;

5 X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals, halides, alkoxides, amides and phosphides:

10 A is an optional bridging group bridging L₃ and L₄;

with alumoxane.

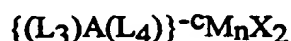
15 23. The composition of claim 22 wherein the alumoxane is methylalumoxane.

24. The composition of claim 22 wherein the ancillary ligand system {(L₃)A(L₄)} has a weight average molecular weight of about or greater than 100 grams/mole.

20

25. The composition of claim 22 wherein the first component is selected from the group consisting essentially of tris(pyrazolyl)borato vanadium oxide dichloride, cyclopentadienyl)vanadium(p-tolyimido)dichloride, Cp*(C₂B₉H₁₁)TaMe₂, wherein Cp* is C₅Me₅,
 25 (C₂B₉H₁₁)W=NAr¹(Me)(Cl), wherein Ar¹ is 2,6-dimethylbenzene, W(=NAr²)₂(CH₂SiMe₃)₂, wherein Ar² is 2,6-diisopropylbenzene, CpNb=N(2,6-diisopropylbenzene)Me₂.

26. A process of preparing the composition of claim 22 comprising
 30 reacting a first component comprising the transition metal complex represented by the formula:



wherein:

35 M is group 5 or 6 transition metal in its highest oxidation state;
 n is the group number of the metal;

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L₃ and L₄ are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the metal;

X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, halogen-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals, halides, alkoxides, amides and phosphides:

A is an optional bridging group linking L₃ and L₄; with an alumoxane.

10 27. The composition of claim 1,3 or 22 placed on a support.

28. The composition of claim 27 prepolymerized.

15 29. A process to produce polyolefins comprising contacting one or more olefins containing from 2 to 20 carbon atoms under polymerization conditions with the composition of claim 1,3 or 22.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/06268

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08F4/74; C07F17/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F ; C07F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	J. AM. CHEM. SOC vol. 113, 1991, pages 893893 - 902 BARBARA J. THOMAS 'Paramagnetic alkylchromium compounds as homogeneous catalysts for the polymerization of ethylene'	
P, X	EP, A, 0 509 294 (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 21 October 1992 see claim 5; example 5 see page 4, line 43 - page 5, line 5	1-6
P, X	US, A, 5 162 466 (FREDERICK J. KAROL) 10 November 1992 see comparative example 10	1
- / - -		
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
13 OCTOBER 1993	21. 10. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	FISCHER B.R.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,X	EP,A,0 495 375 (THE DOW CHEMICAL COMPANY) 22 July 1992 see examples 1,2 -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9306268
SA 76674

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13/10/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0509294	21-10-92	None	

US-A-5162466	10-11-92	CA-A- 2086448	01-07-93
		EP-A- 0550075	07-07-93

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		AU-A- 1023392	23-07-92
		JP-A- 5086120	06-04-93

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